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Interactions Between Bromine and Chlorine in a Pilot-Scale Hazardous Waste Incinerator

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ABSTRACT

Experiments were performed in a 73 kW (250,000 Btu/hr) pilot-scale rotary kiln incinerator simulator equipped with a 73 kW (250,000 Btu/hr) secondary combustion chamber during which a complex organic mixture containing bromine (Br) and chlorine (Cl) was incinerated. Detailed measurements of products of incomplete combustion (PICs) were made, including volatile and semi-volatile organics, as well as polychlorinated and polybrominated dibenzo-p-dioxins and dibenzo furans (PCDDs/PCDFs and PBDDs/PBDFs) as well as mixed bromo-chloro dioxins and furans (MBCDDs/MBCDFs). Results indicated that the ratios of some analogous brominated to chlorinated PICs were greater than the ratios of the amount of Br to Cl in the feed stream. Of particular importance is the potential for this phenomenon to confound the measurement of emissions of total polyhalogenated dibenzo dioxins/furans by promoting formation of PBDDs/PBDFs and MBCDDs/MBCDFs (compounds that are typically not included in regulatory or risk-assessment calculations) at the expense of PCDDs/PCDFs.

INTRODUCTION

A significant amount of concern from both the public and the U.S. Environmental Protection Agency (EPA) has been directed at the formation and control of polychlorinated dibenzo-p-dioxins and dibenzo furans (PCDDs/PCDFs) from combustion systems. These chemicals are believed to be carcinogenic and have been implicated in other potential health effects, such as endocrine disruption (Okey et al., 1994). Bromine (Br), although not nearly as ubiquitous as chlorine (Cl) in combustion systems, undergoes a similar set of reactions as Cl,

and has the potential to form a similar set of compounds, polybrominated dibenzo-p-dioxins and dibenzo furans (PBDDs/PBDFs). In addition, there are an additional 5020 congeners of the mixed bromo-chloro dioxins and furans MBCDDs/MBCDFs. Little is known about the toxicity of PBDDs and PBDFs; however, it is believed to be comparable to that of their chlorinated analogs (Nagao et al., 1990), and very little is known about the mixed bromo-chloro compounds. In fact, few standards exist even for analytical purposes.

BACKGROUND

A significant amount of work is ongoing in Europe, examining the potential for emissions of PBDDs/PBDFs from combustion of materials containing brominated flame retardants. Luijk and Govers (1992) observed both condensed-phase and gas-phase mechanisms of formation of PBDD/PBDF compounds in pyrolysis experiments at the laboratory-scale, with a peak PBDD/PBDF yield occurring at approximately 600 °C. Zelinski et al. (1993) found significant levels of PBDDs/PBDFs in the residues from house fires.

The formation of PBDDs/PBDFs has been observed to utilize some of the same organic precursors that have been implicated in the formation of PCDDs/PCDFs. In a series of laboratory-scale experiments, Sidhu et al. (1995) observed significant gas-phase formation of PBDDs/PBDFs from brominated phenol precursors in laboratory-scale experiments. Gas-phase PBDD/PBDF formation rates were several orders of magnitude higher than gas-phase PCDD/PCDF formation rates, and appeared to have a maximum rate at around 500 °C. Bromine has also been shown to react heterogeneously with organic material bound on particulate matter to form PBDDs/PBDFs. Luijk et al. (1994) has observed at a laboratory-scale the competition of Br and Cl in the de novo synthesis of dioxins and furans, and has also observed the exchange of Br for Cl in 2,3,7,8-tetrabromo dibenzo-p-dioxin. He also found that hydrogen bromide (HBr) appeared to be more reactive than hydrogen chloride (HCl) at halogenating the dioxin and furan structures. This observation is particularly significant. The Deacon reaction (Deacon, 1863),



has been implicated in the formation of PCDDs/PCDFs and it may be that the analogous reaction with HBr is contributing Br₂ for the bromination of the PBDDs/PBDFs. It is well established that the ratio of Br₂ to HBr in the combustion off-gases is much higher than the ratio of Cl₂ to HCl. Although Br is not found in as high concentrations as Cl in common waste streams, such as municipal solid waste, levels of brominated and mixed bromo-chloro phenols have been measured in the flue gases of a municipal waste combustor (MWC) (Heeb et al., 1995), and their levels were of the same order of magnitude as the chlorinated phenols. PBDDs/PBDFs have been measured in MWC flyash (Chatkittikunwong and Creaser, 1994; Sovocoll et al., 1988) at levels approximately an order of magnitude lower than the PCDDs/PCDFs. Noteworthy is that the lower brominated congeners (mono-, di-,

tri-, and tetra- brominated) were predominantly found as opposed to the predominance of the higher chlorinated congeners. This may be due to a steric effect of the larger Br atoms.

The overall findings from the literature appear to support the following observations:

- Addition of Br significantly increases the number of different products of incomplete combustion (PICs).
- Br may compete with Cl for available reactive sites, shifting the concentration of chlorinated PICs.
- Brominated PICs can be preferentially formed and then later have the Br displaced by the Cl, shifting the concentration of chlorinated PICs.

EXPERIMENTAL

The EPA's National Risk Management Research Laboratory (NRMRL), Air Pollution Prevention and Control Division (APPCD), Air Pollution Technology Branch (APTB) is performing research in support of EPA's Office of Solid Waste (OSW) Combustion Strategy. Tests were ongoing to help develop a target analyte list for PICs from hazardous waste incinerators. Based on the potential to form brominated and mixed chloro-bromo compounds when Br is incinerated, the data were re-analyzed from a set of experiments during which a 73 kW (250,000 Btu/hr) pilot-scale rotary kiln incinerator simulator (RKIS) equipped with a 73 kW (250,000 Btu/hr) secondary combustion chamber (SCC) was used to incinerate a complex organic mixture containing Br and Cl. Detailed measurements of PICs were made, including volatile and semi-volatile organics. The analysis and evaluation of results are as yet incomplete. This paper presents preliminary results of the evaluations for chlorinated and brominated PICs including PCDDs/PCDFs and PBDDs/PBDFs.

The EPA/APPCD RKIS facility is located in the EPA Environmental Research Center hazardous waste incineration research laboratory in Research Triangle Park, NC. The facility has a Resource Conservation and Recovery Act (RCRA) Research, Development, and Demonstration (RD&D) permit to burn actual and surrogate hazardous waste. The RKIS was designed to contain the salient features of full-scale kilns, but still be sufficiently versatile to allow parametric experimentation by varying one parameter at a time or controlling a set of parameters independently. The RKIS contains a kiln section, a transition section, and an SCC. The 73 kW (250,000 Btu/hr) prototype rotary kiln thermal destruction unit equipped with a 73 kW (250,000 Btu/hr) SCC was designed for the testing of liquid and solid surrogate hazardous waste materials, and is shown in Figure 1. This facility has been described in detail elsewhere (Linak et al., 1987a, 1987b). The rotating kiln section contains a 0.610 m (24 inch) long, 0.763 m (30 inch) diameter recess which contains the solid waste during incineration. The recess was designed with a length to diameter (L/D) ratio of 0.8, which is 20 to 25 % of a full-scale system.

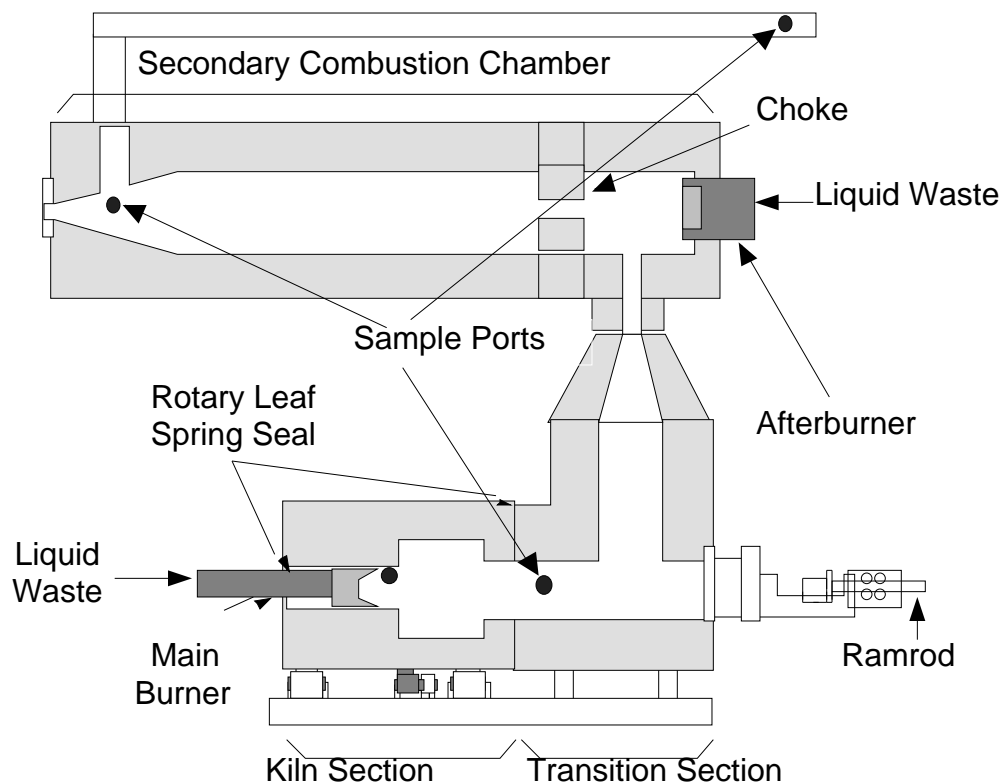


Figure 1. Rotary kiln incinerator simulator

The main burner, based on an International Flame Research Foundation (IFRF) variable swirl design, is the primary heat source to the system. Natural gas is used as the primary fuel during startup and idle.

Prior to sampling, the burner feed was switched to surrogate waste feed and allowed to stabilize for at least 15 minutes prior to sampling. The primary chamber (kiln section) rests on two trunion assemblies and is driven by a motor and gear drive. Consistent rotational speeds between 0.4 and 4.5 rpm are possible. Seals between the kiln and the transition section and main burner extension are made with Teflon-gasketed rotary leaf springs. From the kiln section, the combustion gases enter the transition section.

The gases then flow through the transition section into the SCC. The transition section contains sampling ports and a mechanical ram feeder for charging solid or containerized wastes into the kiln. The SCC consists of three regions: the 0.610 m (24 inch) diameter mixing chamber, the 0.610 m (24 inch) diameter plug flow section, and the stack transition section. A replaceable choke section separates the mixing chamber from the plug flow section. Currently, the installed choke has a 15.24 cm (6 inch) diameter. A conical refractory insert has been installed into the first plug flow sub-section to provide a gradual divergence from the choke diameter to the plug flow section diameter and minimize recirculation zones downstream of the choke. The afterburner, also based on an IFRF variable swirl design, provides heat and flame to this SCC, and is also fired with natural gas during startup and idle times, then switched to the liquid surrogate waste during the tests.

The surrogate hazardous waste feedstock contained representative compounds from many common classes of organic hazardous wastes. Table 1 lists the composition of the surrogate waste feed. Note that too much dibromomethane was inadvertently added in Run 10, resulting in a Br mass percent three times the intended level.

Table 1. Waste Feed Composition			
Class	Compound	Formula	Mass %
carrier liquid	No. 2 fuel oil	n/a	50.0
chlorinated non-aromatic	methylene chloride	CH ₂ Cl ₂	15.93
	chloroform	CHCl ₃	8.94
	carbon tetrachloride	CCl ₄	4.79
chlorinated aromatic	monochlorobenzene	C ₆ H ₅ Cl	6.65
	dichlorobenzene	C ₆ H ₄ Cl ₂	7.69
	chlorophenol	C ₆ H ₅ ClO	3.00
non-chlorinated aromatic	toluene	C ₇ H ₈	10.40
	xylene	C ₈ H ₁₀	10.43
alcohol	isopropanol	C ₃ H ₈ O	4.71
ketone	methyl ethyl ketone	C ₄ H ₈ O	9.67
nitrated waste	pyridine	C ₅ H ₅ N	11.79
PAH	naphthalene	C ₁₀ H ₈	3.00
brominated waste	bromoform	CHBr ₃	1.50
	ethylene dibromide	C ₂ H ₄ Br ₂	1.50*

* - on Run 10, too much ethylene dibromide was inadvertently added

In addition to the organic surrogate waste, an aqueous mixture of metals, including zinc nitrate hexahydrate, nickel nitrate hexahydrate, and copper nitrate hexahydrate, was also fed into the kiln by atomizing an aqueous solution into the main burner. The purpose of the metals injection was to provide a representative supply of metal catalyst to promote any heterogeneous reactions forming PCDDs/PCDFs.

The liquid surrogate waste was pumped into both the primary burner and afterburner. The liquid was metered using calibrated rotameters. The entire liquid feed system was tied into the existing RKIS flame safety interlock system so that the waste feed would be cut off if the RKIS main or afterburner flame was extinguished.

Several different operating conditions were used. The operating conditions were selected to simulate several operating modes for the incinerator system, including sub-optimal combustion. The nominal targeted operating conditions used are listed in Table 2. These represent an excerpt from all of the targeted operating conditions, since analytical results are not available from all tests yet.

Table 2. Nominal Target Operating Conditions

Run	Date	Description
5	5/3/95	Baseline conditions, Kiln T 800 °C, SCC T 1000 °C
6	5/4/95	Baseline conditions, Kiln T 800 °C, SCC T 1000 °C
9	5/12/95	Low SCC temperature, Kiln T 800 °C, SCC T 650 °C
10*	5/16/95	Low SCC temperature, Kiln T 800 °C, SCC T 650 °C
13	8/14/95	Kiln T 800 °C, SCC T 1000 °C, SCC stoichiometric ratio 0.9
14	8/16/95	Kiln T 800 °C, SCC T 1000 °C, SCC stoichiometric ratio 0.9

* - on Run 10, too much ethylene dibromide was inadvertently added

The RKIS was equipped with a continuous gas analysis and data acquisition system consisting of two sets of continuous emissions monitors (CEMs) for oxygen (O₂), carbon monoxide (CO), carbon dioxide (CO₂), nitric oxide (NO), and total hydrocarbons (THCs). This setup allows simultaneous monitoring of gas-phase species at both the kiln exit and the SCC exit.

In addition to the continuous and semi-continuous measurements made on the RKIS, EPA standard sampling methodologies were also used. Volatile organics (VOCs) were measured using two different methods: Method 18 and by Volatile Organics Sampling Train (VOST). Semivolatile organics (SVOCs) were measured using Modified Method 5. PCDDs/PCDFs and PBDDs/PBDFs were measured using Method 23 sampling techniques. The duct temperature at the sampling point, although initially targeted to be identical throughout all tests, was not able to be independently controlled as planned, and so was found to vary between 250 and 350 °C.

The VOST and Tedlar bag samples collected were analyzed by gas chromatography/mass spectrometry (GC/MS) following the procedures described in SW-846 Methods 5040 and 8240. This method is suitable for the analysis of both sample types. Method 8240 quantifies compounds with boiling points ranging from ~30 to ~200 °C, encompassing the capabilities of both sampling methods. The MM5 samples were analyzed in general accordance with SW-846 Method 8270. PCDDs/PCDFs were analyzed by an approach based on EPA Methods 8280 and 23. The analyses were performed by low resolution mass spectrometry (LRMS) with high resolution gas chromatography.

The PCDD/PCDF sample extracts were also analyzed to screen for the presence of PBDDs/PBDFs and MBCDDs/MBCDFs. Standardized analytical techniques for these target compounds do not exist. The analysis for MBCDDs/MBCDFs is particularly hindered by the paucity of both isotopically labeled and unlabeled commercial standards. Three native bromo-chloro standards were used in this case. Because of the lack of some standards, the screening approach targeted only those PBDD/PBDF and MBCDD/MBCDF isomers for which standards had been

obtained. These included compounds with the formulas: BrCl₃DD, Br₂Cl₂DD, Br₄DD, Br₅DD, BrCl₃DF, Br₄DF, and Br₅DF. Samples were analyzed by LRMS using isotope dilution techniques similar to those used to analyze for PCDDs/PCDFs. Prior to extraction, the samples were spiked with known amounts of isotopically labeled Br₄DD and Br₄DF. These were used, along with a recovery standard added before sample cleanup, as internal standards to quantify the target native PBDDs/PBDFs and MBCDDs/MBCDFs as well as assess method performance.

RESULTS

C₁ and C₂ Halogenated Volatile Organics

The results of analysis for halogenated C₁ and C₂ VOCs are listed in Table 3. The list contains possible chloro, bromo, and bromo-chloro organics with one or two carbons. When more than one column is present for a given run, it reflects multiple VOST tube sets. The first column indicates if the compound was in the initial Method 8240 target analyte list or whether it was a tentatively identified compound (TIC) as determined by a mass spectral search. Note that methylene chloride (CH₂Cl₂) was found as a contaminant in some of the blanks, possibly as a laboratory contaminant. It is also not known why the chloromethane concentration was so high on one of the VOST tubes for Run 5. An interesting observation is that, with few exceptions, almost all of these possible compounds were detected in at least one of the runs. If the data are further analyzed, by simply averaging the concentrations of all identified compounds for all of the reported runs, Figure 2 can be constructed. Figure 2 shows the concentrations of some of the halogenated C₁ and C₂ compounds grouped together with the chlorinated and brominated analogs compared side-by-side. Note that the concentrations of the brominated and chlorinated analogs are similar in most cases, even though Br was present in the feed at a mass fraction of only about 10 % of the level of the Cl. This observation indicates that the presence of relatively small amounts of Br can potentially produce quantities of brominated PICs at levels comparable to those of the chlorinated PICs. Table 3 also shows that significant quantities of mixed bromo-chloro PICs were also measured. These low carbon halogenated PICs are participants in aromatic ring growth reactions leading to the larger organic PIC molecules, such as the chlorinated benzenes and phenols, and possibly dioxins and furans.

Aromatic Halogenated VOCs

Table 4 lists the concentrations of the aromatic VOCs found in the tests. Although the aromatic compounds are not identified as commonly throughout all the runs as the smaller molecules were, a similar pattern is found. The data from Run 10, which had the increased Br feed concentration, show the highest concentration and highest number of identified aromatic brominated and bromo-chloro PICs. The concentrations of brominated compounds are generally on the same order of magnitude as their chlorinated analogs.

Table 3. C₁ and C₂ Halogenated VOC Results (all concentrations in µg/m³)

T ⁺ Test Condition Run	Baseline				Low SCC Temp			SCC Fuel Rich			
	5	5	6	6	9	9	10*	13	13	13	14
Y chloromethane	32.6	2100.2	2	3.2	3.9	21.4	2.8	30.6	4.3	13.9	3.5
Y bromomethane	71.4	323.5	6.2	9.2	8.7	46.4	1.8	4	0	2.9	2.4
Y dichloromethane	8.9	44.8	42.7	95.8	5.1	1.5	2.3	13.5	6.9	11.1	13.6
Y dibromomethane	2.5	0.2	0.8	1.8	2.8	4.7	208.1	2	0	3.2	0.8
Y [#] bromochloromethane	0	0	0	0	0	0	0	0	0	0	0
Y trichloromethane	8.8	23.1	26.7	21.3	11	8.8	6.6	2.7	1.1	2.5	4.8
Y tribromomethane	32.2	1.2	19.4	42	42.6	103.4	845.9	0.5	0	0	0.4
Y bromodichloromethane	3.7	1.1	2.6	1.8	25.6	44.6	170.9	2.9	0.8	2.8	4.4
Y dibromochloromethane	5.7	0.4	3.3	8.6	25.3	61.5	230.9	0.9	0	0.3	2.1
Y tetrachloromethane	10.8	2.5	22.7	15.6	200.4	104.4	308.3	2	0	2.2	1.9
N tetrabromomethane	0	0	0	0	0	0	0	0	0	0	0
N bromotrichloromethane	0	0	0	0	12.3	12.1	42.1	0	0	0	0
N dibromodichloromethane	0	0	0	0	0	0	0	0	0	0	0
N tribromochloromethane	0	0	0	0	0	0	0	0	0	0	0
N chloroethyne	0	0	0	0	0	0	0	0	26	37.4	10.6
N bromoethyne	0	0	0	0	0	0	0.8	7	6.3	26.9	9.1
N dichloroethyne	0	0	0	0	0	0	0	0	0	0	0
N dibromoethyne	0	0	0	0	0	0	0	0	0	0	0
N bromochloroethyne	0	0	0	0	0	0	0	0	0	19.4	2.3
Y chloroethene	0.3	3.1	0.1	0.3	6.2	16.3	43.8	6.1	2.3	5	3.6
N bromoethene	0	0	0	0	0	0	2.6	0	0	0	0
Y dichloroethene (total)	0.4	14.6	0	0.3	51.3	73.1	17.9	2.3	0	3.1	5.2
N dibromoethene	0	0	0	4.2	0	0	0.8	0	0	0	6.7
N bromochloroethene	0	0	0	0	0	4.6	46.7	4.4	0	0	0
Y trichloroethene	1.4	2	0.4	0.6	37.2	43	99.6	30.1	0	43	32.5
N tribromoethene	0	0	0	0	0	0	3.1	13.3	0	12.1	9.1
N bromodichloroethene	0	0	0	0	0	0	0	0	0	0	38.6
N dibromochloroethene	0	0	0	0	0	0	0	26.9	0	17.6	25.9
Y tetrachloroethene	2.7	8.2	1.5	2.2	0	0	0	0	0	0	31.9
N tetrabromoethene	0	0	0	0	0	0	0	0	0	0	0
N bromotrichloroethene	0	0	0	0	3.4	1.4	0	0	0	0	0
N dibromodichloroethene	0	0	0	0	0	0	5.2	62.7	0	34.4	28.9
N tribromochloroethene	0	0	0	0	0	0	0	0	0	0	9.5
Y chloroethane	1.1	13.9	0.4	0.5	1.1	0.5	0.1	0.4	0	0	0.4
N bromoethane	0	0	0	0	0	0	0	0	0	0	0
Y dichloroethane	0.2	1.3	0.4	0.5	0.2	0.1	1	1.4	0.9	1.8	1
Y dibromoethane	3	0.1	8	4.6	1.3	2.5	113.5	2	0.3	3.2	0.5
N bromochloroethane	0	0	0	4.5	10.5	4.5	187.2	7.9	0.4	0	0
Y trichloroethane	0.9	0	0.5	0.7	0.1	0	0.2	0	0	0	0
N tribromoethane	0	0	0	0	0	0	0	0	0	0	0
N bromodichloroethane	0	0	0	0	0	0	0	0	0	0	0
N dibromochloroethane	0	0	0	0	0	0	0	0	0	0	0
Y tetrachloroethane	0	0	0.3	0.1	101.1	93.1	0	33.7	0	0	0
N tetrabromoethane	0	0	0	0	0	0	0	0	0	0	0
N bromotrichloroethane	0	0	0	0	0	0	0	0	0	0	0
N dibromodichloroethane	0	0	0	0	0	0	0	0	0	0	0
N tribromochloroethane	0	0	0	0	0	0	0	0	0	0	0

+ - indicates compounds on the Method 8240 target analyte list

- bromochloromethane is an internal standard also found as a PIC -- cannot be quantified

* - on Run 10, too much ethylene dibromide was inadvertently added

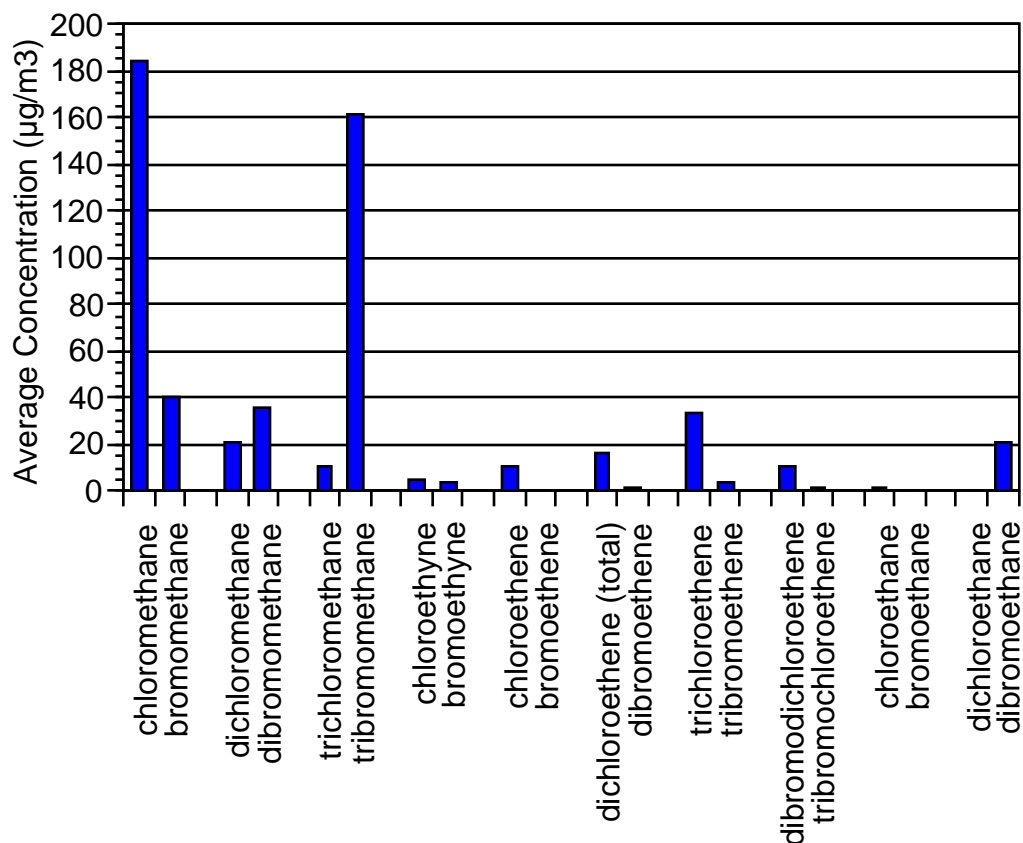


Figure 2. Average concentrations of analogous C₁ and C₂ halogenated compounds

Table 4. Halogenated Aromatic VOC Results (all concentrations in µg/m³)

Test Condition	Baseline				Low SCC Temp			SCC Fuel Rich			
	5	5	6	6	9	9	10*	13	13	13	14
chlorobenzene	4.2	2.7	36.3	14.8	16.8	75.8	8828	3.7	0	13.7	4.7
bromobenzene	0	0	0	0	0	0	13.2	0	0	1.6	0
dichlorobenzene	0	0	3.8	8.1	0	36.7	37.4	3.5	0	2.8	0.9
bromochlorobenzene	0	0	0	0	0	3.9	38.1	0	0	0.6	0
dibromobenzene	0	0	0	0	0	0	4.0	0	0	0	0
trichlorobenzene	0	0	0	0	2.6	8.7	32.7	0	0	0	0
bromodichlorobenzene	0	0	0	0	0	0	5.7	0	0	0	0
dibromochlorobenzene	0	0	0	0	0	0	0	0	0	0	0
tribromobenzene	0	0	0	0	0	0	0	0	0	0	0
bromomethylbenzene	3.0	0	1.3	0	0	0	0	0	0	0	0
bromodimethylbenzene	0	0	5.7	1.6	0	0	0	0	0	0	0

* - on Run 10, too much ethylene dibromide was inadvertently added

Semivolatile Halogenated Organic Compounds

Analysis of the halogenated SVOCs has been qualitative thus far. Table 5 lists the tentatively identified compounds in the semivolatile range. The identifications are based on mass spectral library searches and on GC/MS operator judgment. There appear to be a greater number of brominated compounds than chlorinated in the semivolatile range. It is especially difficult, however, to perform detailed analyses of these compounds, since the analytical methods for identification are not well-defined, and standards are not universally available.

Table 5. Tentatively Identified Halogenated SVOCs

Bromoanthracene	Chloropyridine
Bromobenzene	Dibromoacetic acid, methyl ester
Bromobenzonitrile	Dibromobenzene
Bromochlorobenzene	Dibromochlorobenzene
Bromochlorocyclohexanol	Dibromochlorophenol
Bromocyclohexane	Dibromocyclohexane
Bromocyclohexanol	Dibromodichloroethene
Bromodichlorobenzene	Dibromothiophene
Bromodichlorophenol	Dichloronaphthyridine
Bromomethoxycyclohexane	Tetrabromoethene
Bromomethylbenzene	Tribromobutane
Bromomethylpropane	Tribromochloroethene
Bromonaphthalene	Tribromomethane
Bromotrichlorobenzene	Tribromophenol
Bromotrichloroethene	

Polychlorinated and Polybrominated Dioxins and Furans

Table 6 lists the polychlorinated and polybrominated dioxins and furans found in the tests. Some congeners were found in all tests. These values reflect data taken at duct temperatures ranging from approximately 250 to 350 °C, and reflect short residence time in-flight formation of PCDDs/PCDFs and PBDDs/PBDFs and emissions of those compounds as PICs rather than formation at longer residence times, such as those found in particulate control devices. In general, the low temperature and high Br process conditions tended to yield higher levels of PICs than the baseline and even the fuel rich conditions. Of particular interest is the observation of the very high levels of PCDDs/PCDFs that were found during Run 10, when the Br was at the high feed concentration. Tripling the concentration of Br in the feed resulted in an order of magnitude increase in PCDD/PCDF emissions, plus measured quantities of PBDDs/PBDFs were much higher. It may be that the presence of Br inhibits reactions that reduce the production of PCDDs/PCDFs. It may also be that Br may enhance some of the reactions that produce PCDDs/PCDFs. Further work is planned to investigate this phenomenon. It is also of interest that variations between the different run conditions produced a wide variation in concentrations of PCDDs/PCDFs. These data are

undergoing further analyses to evaluate differences between run conditions. In spite of efforts to maintain a constant duct temperature, variations did occur, and this may be sufficient to account for some of the variations. HCl concentrations in the sampling duct were on the order of 5000 ppmv, which could provide more than sufficient gas-phase Cl to achieve these concentrations of PCDDs/PCDFs. This is not typical of normal incinerator operation, since typically the HCl is removed prior to passing the gases through the optimal PCDD/PCDF formation temperature window.

Table 6. Polychlorinated and Polybrominated Dioxins and Furans

	Baseline		Low SCC Temp		SCC Fuel Ric	
	Run	Run	Run	Run	Run	Run
	5	6	9	10*	13	14
	(ng/m3)	(ng/m3)	(ng/m3)	(ng/m3)	(ng/m3)	(ng/m3)
Monochlorodibenzofuran	0	0	693.79	10944.93	67.38	1.22
Monochlorodibenzodioxin	0	0	16.89	1770.38	0	1.57
Dichlorodibenzofuran	0	0	1145.83	16640.27	52.04	0
Dichlorodibenzodioxin	0	0	35.53	3671.38	0	0
Trichlorodibenzofuran	28.87	0	957.67	8940.27	48.35	0
Trichlorodibenzodioxin	0	0	53.01	4677.70	0	0
Tetrachlorodibenzofuran	28.30	0	421.75	1332.95	39.22	0
Tetrachlorodibenzodioxin	0	0	43.11	29.78	0	0
Pentachlorodibenzofuran	54.34	8.33	358.83	659.23	57.28	0
Pentachlorodibenzodioxin	0	0	43.69	373.04	0	0
Hexachlorodibenzofuran	39.81	0	310.49	470.22	177.09	0
Hexachlorodibenzodioxin	0	0	78.64	386.36	5.63	0
Heptachlorodibenzofuran	47.55	7.04	230.10	206.49	126.99	10.43
Heptachlorodibenzodioxin	7.74	0	73.98	289.18	29.13	0
Octachlorodibenzofuran	16.42	0	535.92	306.49	27.96	14.43
Octachlorodibenzodioxin	56.04	0	553.98	96.51	79.81	8.00
Totals	279	15	5553	50795	711	36
Bromotrichlorodibenzodioxin	0	0	0	90.52	0	0
Bromotrichlorodibenzofuran	0	0	0	0	•	0
Dibromodichlorodibenzodioxin	0	0	0	32.45	0	0
Tetrabromodibenzodioxin	0	0	0	0	0	0
Pentabromodibenzodioxin	0	0	0	0	0	0
Bromotrichlorodibenzofuran	0	0	9.71	295.51	0	0
Tetrabromodibenzofuran	0	0	0	8.49	0	0
Pentabromodibenzofuran	0	0	0	0	0	0

• - Detected, but not quantified

* - on Run 10, too much ethylene dibromide was inadvertently added

CONCLUSIONS

Based on a series of experiments on a pilot-scale rotary kiln incinerator simulator, using a complex surrogate waste mixture containing Cl and Br, several important observations were noted. Brominated C₁ and C₂ PICs were present at higher-than-expected concentrations than their chlorinated analogs, in spite of Br's being present at only 10% of the mass concentration of Cl in the feed. This phenomenon was also observed with aromatic halogenated PICs such as brominated and chlorinated benzenes. A large number of chlorinated, brominated, and bromo-chloro semivolatile organics were also detected. Even though the sampling was performed upstream of a particulate matter control device, and samples were taken after a fairly short residence time in the optimal formation window between 600 and 200 °C, chlorinated, brominated, and chloro-bromo dioxins and furans were detected, and some congeners of the PBDDs/PBDFs were detected. During Run 10, with an erroneously high level of Br in the feed, emissions of PCDDs/PCDFs were dramatically increased, and significant emissions of PBDDs/PBDFs and bromo-chloro dioxins and furans were found. It is not known whether the presence of Br enhances production or inhibits destruction of PCDDs/PCDFs. Additional runs are needed to confirm these results.

It is also unknown whether bromination increases or decreases the relative amounts and toxicities of the PCDD/PCDF, PBDD/PBDF, and MBCDD/MBCDF PICs. If bromination of PICs is additive, then brominated compounds (e.g., PBDDs/PBDFs), could add significantly to risk assessment calculations, especially if emissions of PBDDs/PBDFs are at a similar concentration as PCDDs/PCDFs. If the process is substitutive, Br could bring into question trial burn and compliance test PCDD/PCDF results due to bromination of chlorinated PICs resulting in brominated or bromo-chloro PICs that aren't considered in risk assessment calculations. Further work is planned so that these phenomena can be better quantified and explained.

The results from these tests have implications regarding incinerator trial burns and compliance tests. They raise the following questions:

- Can compliance with potential PCDD/PCDF emission limits that have been demonstrated in a trial burn using a synthetic POHC feed with no Br in the system be ensured, during operation when Br is present?
- Should Br be added to the system during trial burns to challenge the system, even though brominated organics, including PBDDs/PBDFs, are not included in the regulations or the risk assessment calculations?
- How can PICs such as PBDDs/PBDFs be accounted for if their sampling and analytical methodologies have not been validated?

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